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1 RECORDING MEDIUM, INK-JET RECORDING METHOD USING
 THE SAME, AND DISPERSION OF ALUMINA HYDRATE

BACKGROUND OF THE INVENTION

5 Field of the Invention

 The present invention relates to a recording medium
suitable for use in recording using water-based inks, ink-
jet recording method and a dispersion. In Particular,
this invention relates to a recording medium which can
10 provide images high in optical density, bright in color
tone and high in resolution, and has excellent ink-
absorbing capacity, an ink-jet recording method using such
a recording medium, and a dispersion of an alumina
hydrate, which is suitable for use in production of the
15 recording medium.

Related Background Art

 In recent years, an ink-jet recording system, in
which minute droplets of an ink are flown by any of
various working principles to apply them to a recording
20 medium such as paper, thereby conducting recording of
images, characters and/or the like, has been quickly
spread as a recording apparatus for various images in
various applications including information instruments
because it has features that recording can be conducted at
25 high speed and with a low noise, color images can be
formed with ease, recording patterns are very flexible,

1 and development and fixing process are unnecessary.

Further, it begins to be applied to a field of recording
of full-color images because images formed by an multi-
color ink-jet recording system are comparable in quality
5 with multi-color prints by a plate making system and
photoprints by a color photographic system, and such
records can be obtained at lower cost than the usual
multi-color prints and photoprints when the number of
copies is small. With the improvement in recordability,
10 such as speeding up and high definition of recording, and
multi-coloring of images, recording apparatus and
recording methods have been improved, and recording media
have also been required to have higher properties.

In order to satisfy such requirements, a wide
15 variety of recording media have been proposed. For
example, Japanese Patent Application Laid-Open No. 52-
53012 discloses paper for ink-jet, in which a base paper
web low in sizing degree is impregnated with a surface
coating. Japanese Patent Application Laid-Open No. 53-
20 49113 discloses paper for ink-jet, in which a sheet
containing urea-formalin resin powder therein is
impregnated with a water-soluble polymer. Japanese Patent
Application Laid-Open No. 55-5830 discloses paper for ink-
jet recording, in which a coating layer having good ink
25 absorptiveness is provided on a surface of a base.
Japanese Patent Application Laid-Open No. 55-51583

1 discloses that amorphous silica is used as a pigment in a
coating layer. Japanese Patent Application Laid-Open No.
55-146786 discloses that a coating layer formed of a
water-soluble polymer is used.

5 In U.S. Patent Nos. 4,879,166 and 5,104,730, and
Japanese Patent Application Laid-Open Nos. 2-276670, 4-
37576 and 5-32037, there have been proposed recording
sheets having a layer using an alumina hydrate of a
pseudoboehmite structure.

10 As described in U.S. Patent Nos. 4,374,804 and
5,104,730, and Japanese Patent Application Laid-Open Nos.
58-110287 and 4-37576, it has also been conducted to form
an ink-receiving layer of a multi-layer structure using a
silica or alumina material.

15 However, the conventional recording media have
involved the following problems:

1) U.S. Patent No. 5,104,730, and Japanese Patent
Application Laid-Open Nos. 2-276670, 2-276671 and 3-275378
disclose recording media having extremely narrow
20 distribution of pore radius. As disclosed in Japanese
Patent Application Laid-Open Nos. 4-267180 and 5-16517,
however, individual dyes for inks (cyan, magenta, yellow
and black) and solvents for the inks are selectively
adsorbed in pores of a specific size. Therefore, bleeding
25 may occur on prints if the composition of ink is changed.

The bleeding refers to a phenomenon that edges of

1 boundaries of multi-color printed areas can not be
resolved because of feathering caused when ink is still
fluid before it is fixed in the ink-receiving layer.

2) U.S. Patent No. 5,104,730, and Japanese Patent
5 Application Laid-Open Nos. 2-276670, 2-276671 and 3-275378
disclose recording media having pore radius distribution
as narrow as 10 to 30 Å in average pore radius. In this
pore radius distribution, dye adsorptiveness is good,
while the absorptiveness of solvent is insufficient,
10 resulting in the occurrence of beading.

The beading mentioned in the present invention
refers to a phenomenon in which dots irregularly move in
the plane direction of the surface of an ink-receiving
layer when ink is still fluid before it is fixed in the
15 ink-receiving layer, thus forming new aggregates together
with adjacent dots to cause an unevenness in the density
of recorded images.

3) In printing of color images, inks increase in
quantity. The inks printed cannot be completely absorbed
20 in pores, but run out on the surface of an ink-receiving
layer, so that bleeding occurs, resulting in deterioration
in print quality.

4) High-speed printing requires to have good drying
ability. However, absorbing rate is insufficient, and the
25 printed surface is hence not dry when discharged out of a
printing apparatus, so that output images may be possibly

1 impaired by contact.

5) There is a problem that the solids concentration
of a dispersion of a pigment or the like cannot be
increased because the viscosity of the dispersion
5 increases with time, resulting in a failure to apply it.
As a measure for the solution of the problem, Japanese
Patent Application Laid-Open No. 4-67986 discloses a
process in which the polymerization degree of a polymer as
a binder is lowered. However, this process involves
10 problems of defective appearance such as cracking in an
ink-receiving layer, reduction in water fastness, and the
like, and hence still requires a further improvement.

6) There is a problem that since the viscosity of
the dispersion is high, its solids concentration cannot be
15 increased. As a measure for the solution of the problem,
Japanese Patent Application Laid-Open No. 4-67985
discloses a process in which an acid such as a
monocarboxylic acid is added as a dispersant. However,
this process is accompanied by productive problems that
20 offensive odor is given, and corrosion is caused.

7) In order to improve ink absorptiveness and
resolution of images, U.S. Patent Nos. 4,780,356,
4,374,804 and 5,104,730, Japanese Patent Publication No.
3-72460, and Japanese Patent Application Laid-Open Nos.
25 55-11829, 58-110287, 62-270378 and 4-37576 disclose a
process in which an ink-receiving layer of a two or more

1 multi-layer structure is formed. However, the process
involves a problem that coating and drying must be
conducted at least twice for forming the ink-receiving
layer, and so the number of processes increases. In
5 addition, since the physical property values of the
individual layers are different from each other, there are
also problems of changes with time, defective appearance
such as cracking in the ink-receiving layer, and
separation and peeling of the layers from each other upon
10 printing or the like.

8) Japanese Patent Application Laid-Open No. 3-
281384 discloses an alumina hydrate forming an aggregate
like a needle, which is in the form of a column having an
aspect ratio of not higher than 3 and unidirectionally
15 oriented, and a process for forming an ink-receiving layer
using the alumina hydrate. However, since particles of
the alumina hydrate are oriented and compacted, spaces
among the alumina hydrate particles in the ink-receiving
layer tends to narrow. Therefore, the pore radius is
20 partial to a narrow side, and distribution of pore radius
has a tendency to narrow. As a result, there is a problem
that beading occurs as described above.

SUMMARY OF THE INVENTION

25 The present invention has thus been made with a view
toward solving the above problems and has as its object

1 the provision of a recording medium which can be suited to
inks of various compositions, is excellent in ink
absorptiveness, can suppress feathering or bleeding of
print and occurrence of beading and can provide images
5 high in optical density, and an ink-jet recording method
using this recording medium.

Another object of the present invention is to
provide a recording medium which can effectively adsorb or
absorb a dye and a solvent, which are components for an
10 ink, and hence permits good coloring and quick drying, and
an ink-jet recording method using this recording medium.

A further object of the present invention is to
provide a dispersion of a pigment, which is suitable for
use in production of the above recording media.

15 A still further object of the present invention is
to provide a recording medium in which both dispersibility
of a dispersion for coating and dye-adsorbing ability are
satisfied, an ink-jet recording method using the recording
medium, and a dispersion suitable for use in production of
20 the recording medium.

The above objects can be achieved by the present
invention described below.

According to the present invention, there is thus
provided a recording medium comprising an alumina hydrate
25 having an average pore radius of 20 to 200 Å and a half
breadth of pore radius distribution of 20 to 150 Å.

1 According to the present invention, there is also
provided a recording medium comprising a base material and
an ink-receiving layer which comprises a pigment and a
binder and is provided on the base material, wherein the
5 pigment is an alumina hydrate and the ink-receiving layer
has an average pore radius of 20 to 200 Å and a half
breadth of pore radius distribution of 20 to 150 Å.

 According to the present invention, there is further
provided a recording medium comprising principally pulp
10 fibers and a filler, wherein the filler comprises an
alumina hydrate having an average pore radius of 20 to 200
Å and a half breadth of pore radius distribution of 20 to
150 Å.

 According to the present invention, there is still
15 further provided a recording medium comprising an alumina
hydrate having at least two peaks in pore radius
distribution.

 According to the present invention, there is yet
still further provided a recording medium comprising a
20 base material and an ink-receiving layer which comprises a
pigment and a binder and is provided on the base material,
wherein the pigment comprises an alumina hydrate and the
ink-receiving layer has at least two peaks in pore radius
distribution.

25 According to the present invention, there is still
further provided a recording medium comprising principally

1 pulp fibers and a filler, wherein the filler comprises an
alumina hydrate having at least two peaks in pore radius
distribution.

According to the present invention, there is yet
5 still further provided a recording medium comprising an
alumina hydrate containing 0.01 to 1.00 % by weight of
titanium dioxide.

According to the present invention, there is yet
still further provided a recording medium comprising a
10 base material and an ink-receiving layer which comprises
an alumina hydrate containing 0.01 to 1.00 % by weight of
titanium dioxide and is provided on the base material.

According to the present invention, there is still
further provided a recording medium comprising principally
15 pulp fibers and a filler, wherein the filler comprises an
alumina hydrate containing 0.01 to 1.00 % by weight of
titanium dioxide.

According to the present invention, there is yet
still further provided an ink-jet recording method
20 comprising ejecting minute droplets of an ink from an
orifice to apply the droplets to a recording medium,
thereby conducting printing, wherein one of the recording
media described above is used as the recording medium.

According to the present invention, there is yet
25 still further provided a dispersion of an alumina hydrate,
which is obtained by dispersing an alumina hydrate

1 containing 0.1 to 1.0 % by weight of a nitrate anion and
having an average pore radius of 20 to 200 Å and a half
breadth of pore radius distribution of 20 to 150 Å in
deionized water, wherein the dispersion having a solids
5 concentration of 15 % by weight has a viscosity of not
higher than 75 cP as measured at 20°C and a shear rate of
7.9 sec⁻¹.

According to the present invention, there is yet
still further provided a dispersion of an alumina hydrate,
10 which is obtained by dispersing an alumina hydrate
containing 0.1 to 1.0 % by weight of a nitrate anion and
having at least two peaks in pore radius distribution in
deionized water, wherein the dispersion having a solids
concentration of 15 % by weight has a viscosity of not
15 higher than 75 cP as measured at 20°C and a shear rate of
7.9 sec⁻¹.

According to the present invention, there is yet
still further provided a dispersion of an alumina hydrate,
which is obtained by dispersing a titanium dioxide-
20 containing alumina hydrate containing 0.1 to 1.0 % by
weight of a nitrate anion in deionized water, wherein the
dispersion having a solids concentration of 15 % by weight
has a viscosity of not higher than 75 cP as measured at
20°C and a shear rate of 7.9 sec⁻¹.

25

BRIEF DESCRIPTION OF THE DRAWINGS

1 Fig. 1 is a cross-sectional view of a recording
medium according to the present invention.

 Fig. 2 diagrammatically illustrates an X-ray
diffraction pattern of an alumina hydrate according to the
5 present invention.

 Fig. 3 is a photograph illustrating a crystal
structure of the alumina hydrate according to the present
invention.

 Fig. 4 is a photograph illustrating the structure of
10 particles of the alumina hydrate in an ink-receiving layer
according to the present invention, viewed from the
section of the ink-receiving layer.

 Fig. 5 diagrammatically illustrates an isothermal
adsorption curve of an alumina hydrate used in the first
15 aspect of the present invention.

 Fig. 6 diagrammatically illustrates the pore radius
distribution of the alumina hydrate used in the first
aspect of the present invention.

 Fig. 7 diagrammatically illustrates an isothermal
20 adsorption curve of an alumina hydrate used in the second
aspect of the present invention.

 Fig. 8 diagrammatically illustrates the pore radius
distribution of the alumina hydrate used in the second
aspect of the present invention.

25 Figs. 9A and 9B are cross-sectional views
illustrating a contained type and a mixed type,

1 respectively, of pore portions in recording media in the
third aspect of the present invention.

Fig. 10 diagrammatically illustrates an isothermal
adsorption curve of a titanium dioxide-containing alumina
5 hydrate used in the third aspect of the present invention.

Fig. 11 diagrammatically illustrates the pore radius
distribution of the titanium dioxide-containing alumina
hydrate used in the third aspect of the present invention.

10 DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a recording
medium (first aspect) comprising, as an essential
component, at least an alumina hydrate having the average
pore radius and half breadth of pore radius distribution
15 within the specific ranges described above, a recording
medium (second aspect) comprising, as an essential
component, at least an alumina hydrate having the above-
described feature in pore radius distribution, and a
recording medium (third aspect) comprising, as an
20 essential component, at least an alumina hydrate
containing titanium dioxide in the specific amount
described above. Each of these recording media is
constituted by, for example, internally containing its
corresponding alumina hydrate in a sheet such as paper at
25 a stage in which the sheet is formed from a raw material,
or forming an ink-receiving layer composed principally of

1 the alumina hydrate and a binder on a base material as
illustrated in Fig. 1. The alumina hydrates are most
preferable, in particular, as a material used in the ink-
receiving layer because it has a positive charge, so that
5 a dye in an ink is well fixed and an image good in
coloring is hence provided, and moreover there are no
problems of bronzing and light fastness, which have
heretofore been caused by the use of silica compounds. A
phenomenon called "bronzing" in which the hue of a black
10 recorded area looks brownish has presented itself, and a
new problem has hence been offered.

The alumina hydrates used in the recording media
according to the present invention may preferably be non-
crystalline as analyzed by the X-ray diffraction method.

15 The alumina hydrate is defined by the following
general formula:



wherein n is an integer of 0, 1, 2 or 3, m is a number of
0 to 10, preferably 0 to 5. In many cases, mH₂O
20 represents an aqueous phase which does not participate in
the formation of a crystal lattice, but is able to
eliminate. Therefore, m may take a value other than an
integer. Besides, m may take a value of 0 when a material
of this kind is calcinated.

25 The alumina hydrate can be produced by any
conventional method such as the hydrolysis of aluminum

1 alkoxide or sodium aluminate. Rocek, et al. [Collect
Czech. Chem. Commun., Vol. 56, 1253-1262 (1991)] have
reported that the pore structure of aluminum hydroxide is
affected by deposition temperature, pH of the solution,
5 aging time and a kind of surfactants used.

For example, KODANSHA LTD PUBLISHERS, "Shokubai Koza
(The Catalyst Course)", Vol. 5, Chapter on Engineering,
Design of Catalysts, 123 (1985) describes an alumina
hydrate as generally having one peak in pore radius
10 distribution. Further, Kobayashi ["Surface", Vol. 15, 282
(1977)] has also reported that an alumina hydrate has one
peak in pore radius distribution. Rocek, et al. [Collect
Czech. Chem. Commun., 56(6), 1263-1269 (1991)] have
reported that aluminum hydroxide deposited at a relatively
15 low temperature of 30 to 50°C and pH 7 to 8 shows a two-
peak porous structure having peaks in a large pore region
and a medium pore region.

The shape of the alumina hydrate used in the present
invention is preferably in the form of a flat plate and
20 has an average aspect ratio of 3 to 10 and a slenderness
ratio of a flat plate surface of 0.6 to 1.0. The
definition of the aspect ratio can be given by the method
described in Japanese Patent Publication No. 5-16015. The
aspect ratio is expressed by a ratio of "diameter" to
25 "thickness" of a particle. The term "diameter" as used
herein means a diameter of a circle having an area equal

1 to a projected area of the particle, which has been
obtained by observing the alumina hydrate through a
microscope or a TEM. The slenderness ratio means a ratio
of a minimum diameter to a maximum diameter of the flat
5 plate surface when observed in the same manner as in the
aspect ratio. If the average aspect ratio is lower than
the lower limit of the above range, the range of the pore
radius distribution of the ink-receiving layer narrows.
On the other hand, average aspect ratios higher than the
10 upper limit of the above range makes it difficult to
produce the alumina hydrate with its particle size even.
If the average slenderness ratio is lower than the lower
limit of the above range, the range of the pore radius
distribution similarly narrows. As described in the
15 literature [Rocek J., et al., Applied Catalysis, Vol. 74,
29-36 (1991)], it is generally known that pseudoboehmite
among alumina hydrates has both needle form and another
form.

According to a finding of the present inventor, the
20 alumina hydrate in a flat plate form is more preferred
because it has better dispersibility than that of a needle
form (the ciliary form), and the orientation of particles
of the alumina hydrate becomes random as illustrated in
the photograph in Fig. 4 when forming an ink-receiving
25 layer, so that the range of the pore radius distribution
widens.

1 In Handbook of Paper Processing, p. 402, there is
described particles of aluminum hydroxide as being in the
form of a hexagonal flat plate. Besides this, alumina
hydroxides such as HIGILITE (trade name, product of Showa
5 Denko K.K.) and HYDRAL (trade name, product of ALCOA) are
known. Further, Japanese Patent Application Laid-Open No.
2-276670 discloses an alumina sol in the form of a needle
having an aspect ratio of 2 to 10, while Japanese Patent
Application Laid-Open No. 3-285814 discloses a boehmite
10 sol in the form of a plate having an aspect ratio of 2 to
10. However, none of these documents disclose a
relationship between the shape of the alumina hydrate and
the pore structure or dispersibility of particles thereof
as described below.

15 The BET surface area of each of the alumina
hydrates, the pore radius distributions of the alumina
hydrate and the ink-receiving layer containing the alumina
hydrate, and pore volumes and isothermal adsorption and
desorption curves as described below can be obtained at
20 the same time by the nitrogen adsorption and desorption
method. The BET specific surface areas of the alumina
hydrates used in the present invention may preferably be
within a range of from 70 to 300 m²/g. If the BET
specific surface area is smaller than the lower limit of
25 the above range, the pore radius distribution is partial
to a large side. As a result, a dye in an ink cannot be

1 fully adsorbed and fixed. On the other hand, surface
areas greater than the upper limit of the above range
result in failures to apply the pigment with good
dispersibility and hence to control the pore radius
5 distribution.

No particular limitation is imposed on the
production process of the alumina hydrates used in the
present invention. However, it is preferable to use a
process capable of producing a non-crystal alumina
10 hydrate. For example, either of the Bayer's process or
the alum pyrolysis process may be used.

As a process for the production of the non-crystal
alumina hydrate, which can be particularly preferably used
in the present invention, may be mentioned a process in
15 which an acid is added to an aluminum long-chain alkoxide
to hydrolyze the alkoxide, thereby obtaining an alumina
hydroxide. The term "aluminum long-chain alkoxide" as
used herein means an alkoxide having, for example, 5 or
more carbon atoms. Further, the use of an alkoxide having
20 12 to 22 carbon atoms is preferred because the removal of
alcohol formed and the shape control of the alumina
hydrate can be conducted with ease. The process has an
advantage that impurities such as various ions are hard to
get mixed compared with the process for producing alumina
25 hydrogel or cationic alumina. The aluminum long-chain
alkoxide also has an advantage that since the alcohol

1 formed is easy to remove after the hydrolysis, the removal
of the alcohol from the alumina hydrate can be completely
conducted compared with the case where a short-chain
alkoxide such as aluminum isopropoxide is used. Further,
5 in the process making use of the aluminum long-chain
alkoxide, particles of the alumina hydrate obtained by the
hydrolysis tend to be in the form of a flat plate, and so
the shape of the particles is easy to control. In this
process, it is preferable from a viewpoint of obtaining
10 the non-crystal alumina hydrate to preset the pH of a
solution to 6 or lower upon the initiation of the
hydrolysis. If the pH is more than 8, the alumina
hydrate to be finally obtained will become crystalline.

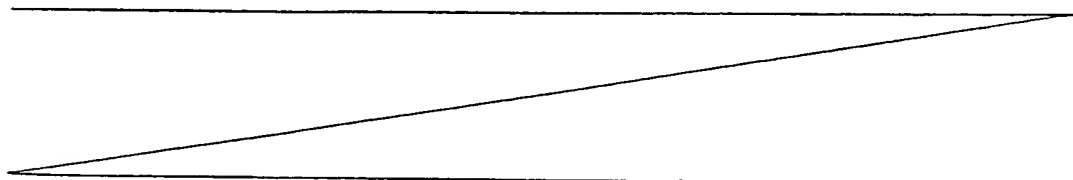
The alumina hydrate used in the first aspect of
15 the present invention obtained by the above process is
subjected to a hydrothermal synthesis to grow its
particles (aging process). The conditions of the aging
process can be suitably adjusted to control the pore form
of the alumina hydrate particles within a specific range.
20 If the time of the aging is too short, primary particles
of the alumina hydrate, which are relatively uneven in
particle size, grow, and so the sizes of spaces among the
primary particles, which the spaces define pores, become
uneven. As a result, it is considered that the range of
25 pore radius distribution widens. The correlation between
the degree of unevenness of the primary particles and the
range of the pore radius distribution is unclear. The sol

1 obtained may be used as a dispersion as it is as disclosed
in Japanese Patent Application Laid-Open No. 2-276670. In
the present invention, it is however preferable to dry the
sol once into powder by a method such as spray drying and
5 then prepare a dispersion. In this case, the
dispersibility of the alumina hydrate in water is more
enhanced.

The best feature of the alumina hydrate used in the
third aspect of the present invention is to contain
10 titanium dioxide in a specific proportion. The content
thereof is preferably within a range of from 0.01 to 1.00
% by weight, more preferably from 0.13 to 1.00 % by
weight. Further, the valence of titanium in the titanium
dioxide is preferably +4.

15 According to another finding of the present
inventor, the titanium dioxide contained exists on the
surface of the alumina hydrate in the form of such
ultrafine particles that they cannot be observed through
an electron microscope of 500,000 magnifications, and
20 serves as an adsorption site upon the adsorption of the
dye in the ink. The reason of that is not clearly
understood. As reported by Yang, et al. [React. Kinet.

25



1 Catal. Lett., 46(1), 179-186 (1992)], it is however
inferred that twisted sites containing strongly electron-
acceptable Al^{3+} are formed by the addition of titanium
dioxide, and the dye-adsorbing ability is hence improved,
5 or the titanium ion of titanium dioxide forms a coordinate
bond with the dye.

According to a further finding of the present
inventor, the valence of the titanium is +4 judged from
the value of bound energy by the observation of ESCA.
10 Since no splitting occurs on 3p peak for titanium and 2p
peak for aluminum, there is no interaction between
titanium and aluminum. Namely, titanium dioxide solely
exists without interacting between titanium and aluminum.
When the surface of the titanium dioxide-containing
15 alumina hydrate is etched with argon, the amount of
titanium is decreased to half in the etching time of about
100 seconds. No titanium is detected in the etching time
of about 500 seconds. Therefore, the titanium dioxide
exists only in the vicinity of the surfaces of the alumina
20 hydrate particles without affecting the surface charge of
the alumina hydrate under the conditions of the particle
size, valence and splitting of peaks, so that the
dispersibility of the alumina hydrate is not impaired.

If the valence of titanium in the titanium dioxide
25 becomes lower than +4, the titanium dioxide comes to serve
as a catalyst by light irradiation and the binder is hence

1 deteriorated, so that cracking and dusting tends to occur.
The alumina hydrate used in the third aspect of the
present invention may contain the titanium dioxide either
only in the vicinity of the surfaces of the alumina
5 hydrate particles or up to the interiors thereof. Its
content may be changed from the surface to the interior.
As demonstrated in Examples of the present invention,
which will be described subsequently, the titanium dioxide
may preferably be contained only in the close vicinity of
10 the surfaces of the particles because the bulk properties
of the interior of the alumina hydrate are easy to be kept
in the vicinity of the surface, thereby undergoing no
change in dispersibility.

Although oxides of magnesium, calcium, strontium,
15 barium, zinc, boron, silicon, germanium, tin, lead,
zirconium, indium, phosphorus, vanadium, niobium,
tantalum, chromium, molybdenum, tungsten, manganese, iron,
cobalt, nickel, ruthenium and the like may be used instead
of the titanium dioxide. However, the titanium dioxide is
20 most preferred from the viewpoint of the adsorptiveness of
a dye in an ink and dispersibility. Most of the oxides of
the above-mentioned metals are colored, while the titanium
dioxide is colorless. From this point, the titanium
dioxide is also preferred.

25 The titanium dioxide-containing alumina hydrate used
in the third aspect of the present invention may

- 1 preferably be of a non-crystalline structure as analyzed by the X-ray diffraction method.

As a process for producing the titanium dioxide-containing alumina hydrate, a process in which a liquid
5 mixture of an aluminum alkoxide and a titanium alkoxide is hydrolyzed is most preferred because the particle size of titanium dioxide can be made small and is easy to control. The particle size and shape in this process are discussed in the form of an $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst by an alkoxide process
10 in, for example, Gakkai Shuppan Center, "Science of Surfaces", edited by Kenji Tamaru, 327 (1985). As another process, its production may also be conducted by adding an alumina hydrate as a nucleus for crystal growth upon the hydrolysis of the mixture of the aluminum alkoxide and the
15 titanium alkoxide. In this process, the titanium dioxide exists only in the vicinity of the surface of the alumina hydrate.

Materials with a variety of materials supported on surfaces of particles such as alumina are widely known in
20 the field of catalysts. Titanium dioxide is poor in solubility in solvents such as water, and hence extremely hard to be supported on alumina or the like. It is known to support titanium as a soluble salt on the surfaces of alumina hydrate particles. It is however difficult to
25 convert the titanium compound supported on the surfaces of the hydrate particles to titanium dioxide and also to

1 remove the counter ion component by which the titanium
salt has been formed. In general, the valence of the
titanium compound supported is smaller than +4.
Therefore, the valence of titanium as determined by ESCA
5 is not +4 like the titanium dioxide-containing alumina
hydrate according to the third aspect of the present
invention.

Dispersions of the above-described alumina hydrates
used in the first to third aspects of the present invention
10 may be used either as an additive (for example, added to a
pulp slurry upon the preparation of a raw material for
paper making) upon the production of the respective
recording media, more specifically, upon the production of
paper, or as a coating dispersion for forming an ink-
15 receiving layer on a base material.

In the recording medium used in the first to third
aspects of the present invention according to an embodiment
of the present invention, a coating dispersion (a
dispersion of the alumina hydrate) containing the alumina
20 hydrate as a pigment and a binder is applied to a base
material to form an ink-receiving layer. The values of
physical properties of the ink-receiving layer are not
determined only by the alumina hydrate, but changed by
various production conditions such as the kind and mixing
25 amount of the binder, the concentration, viscosity and
dispersion state of the coating dispersion, coating
equipment, coating head, coating weight, and the flow

1 rate, temperature and blowing direction of drying air. It
is therefore necessary to control the production
conditions within the optimum limits for achieving the
properties of the ink-receiving layer according to the
5 present invention.

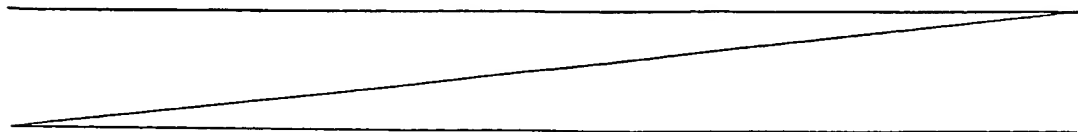
The alumina hydrate used in the first aspect of the
present invention is wide in the half breadth of pore
radius distribution, which will be described subsequently,
and is dispersed up to a level of primary particles in a
10 dispersion for coating. Such wide pore radius
distribution is substantially kept even after the
formation of the ink-receiving layer through steps of
dispersion of the alumina hydrate, coating on the base
material and drying. The reason of this is not clearly
15 understood. The present inventor however dares to explain
for facilitating the understanding of the present
invention, and infers that a pore structure is defined
principally by spaces among the primary particles of the
alumina hydrate, and the alumina hydrate particles in the
20 form of a flat plate are oriented at random in the ink-
receiving layer, or that the wide pore radius distribution
attributable to the unevenness of the particle size of the
alumina hydrate is kept even in the ink-receiving layer.

The average pore radius of the ink-receiving layer
25 is preferably within a range of from 20 to 200 Å, while
its half breadth of pore radius distribution is preferably
within a range of from 20 to 150 Å, more preferably from

1 80 to 150 Å. The term "half breadth of pore radius
distribution" as used herein means a breadth of pore
radius which is a magnitude half of the magnitude of the
average pore radius. If the average pore radius is larger
5 than the upper limit of the above range, the resulting
recording medium is deteriorated in the adsorption and
fixing of a dye in an ink, and so bleeding tends to occur
on images. If the average pore radius is smaller than the
lower limit of the above range, the resulting recording
10 medium is deteriorated in ink absorptiveness, and so
beading tends to occur. On the other hand, if the half
breadth is outside of this range, the resulting recording
medium is deteriorated in the adsorption of a dye or a
solvent in an ink.

15 As with the ink-receiving layer, the pore radius
distribution of the alumina hydrate making up the ink-
receiving layer preferably has an average pore radius of
20 to 200 Å and a half breadth of pore radius
distribution of 20 to 150 Å. The pore radius
20 distribution of the ink-receiving layer depends upon the
pore radius distribution of the alumina hydrate.
Therefore, if the pore radius distribution of the alumina
hydrate is outside the above range, the pore radius

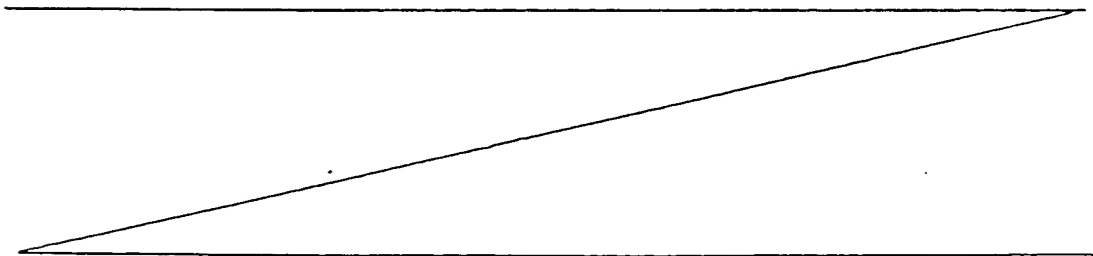
25



1 distribution of the ink-receiving layer cannot be
controlled within the above range.

In the first aspect, the pore volume of the ink-receiving layer is preferably within a range of from 0.4
5 to 0.6 cc/g. If the pore volume of the ink-receiving layer is greater than the upper limit of the above range, cracking and dusting occur on the ink-receiving layer. If the pore volume is smaller than the lower limit of the above range, the resulting recording medium is
10 deteriorated in ink absorption. The total pore volume of the ink-receiving layer is more preferably at least 8 cc/m². If the total pore volume is smaller than this limit, inks tend to run out of the ink-receiving layer when multi-color printing is conducted, and so bleeding
15 occurs on images. As with the ink-receiving layer, the pore volume of the alumina hydrate making up the ink-receiving layer is preferably within a range of from 0.4 to 0.6 cc/g. If the pore volume of the alumina hydrate is outside the above range, the pore volume of the ink-
20 receiving layer cannot be controlled within the above range.

25



1 The alumina hydrate obtained by the above process
is subjected to a hydrothermal synthesis, thereby its
particles grow (an aging step). By controlling the
conditions of this step, the pore form of the alumina
5 hydrate particles can be controlled within a specified
range. Upon setting an aging time suitable, primary
particles of the alumina hydrate having relatively even
particle size grow, so that the sizes of spaces among
the primary particles, which define pores, become even
10 and the range of pore radius distribution becomes
narrow. If the aging time is made longer than that
conditions, the alumina hydrate having two tops in the
pore radius distribution can be obtained. As a result,
a recording medium, in which two tops are made in the
15 pore radius distribution of alumina hydrate, can be
obtained. The sol obtained may be used as a dispersion
as it is as disclosed in Japanese Patent Application
Laid-Open No. 2-276670. In the present invention, it is
however preferable to dry the sol once into powder by a
20 method such as spray drying and then prepare a
dispersion. In this case, the dispersibility of the
alumina hydrate in water is more enhanced.

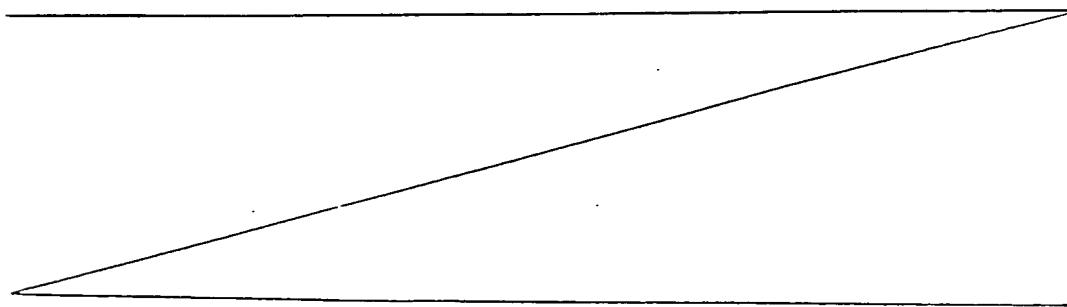
 The alumina hydrate obtained by the process has
two or more peaks in a pore radius distribution. A pore
25 structure is mainly formed by spaces among the primary

1 structure is mainly formed by spaces among the primary
particles of the alumina hydrate. The reason why the
pore radius distribution has at least two peaks is
considered to be as follows. Since the alumina hydrate
5 particles are in the form of a flat plate and the
primary particles are oriented at random in the dried
powder, there are defined spaces of portions in which
primary particles overlap with each other in a direction
of the principal plain of the flat plate and spaces of
10 another portions in which an end face and the principal
plane or another end face overlap with each other.
Thus, two or more peaks in the pore radius distribution
are all caused by the spaces among the primary
particles, and at least one of the pore radii at one
15 peak becomes smaller than the minor axis or major axis
radius of the flat plate surface of the primary
particles, while at least one of the pore radii at
another peaks becomes about several times the minor axis
or major axis radius of the flat plate surface.

20 The alumina hydrate of the present invention is,
as described above, has at least two peaks in the pore
radius distribution. Although such the alumina hydrate
is dispersed up to a level of primary particles in a
dispersion for coating, the radius distribution having
25 at least one peaks is kept substantially even when the
ink-receiving layer is formed through the steps of

1 dispersing of the alumina hydrate, coating onto a
substrate and drying. The reason is considered as
follows: Even in an ink-receiving layer, the primary
particles of the alumina hydrate are oriented in random
5 direction, as shown by the photograph in Fig. 3, and
therefore, as same as in a case of titanium dioxide-
containing alumina hydrate, there are generated spaces
of portions in which primary particles overlap with each
other in a direction of the principal plain of the flat
10 plate through a binder and spaces of another portions in
which an end face and the principal plane or another end
face overlap with each other through a binder, by which
the pore radius distribution having two or more peaks is
kept even when the ink-receiving layer is formed
15 therefrom.

Japanese Patent Application Laid-Open No. 58-110287
discloses a recording sheet having peaks of pore radius at
0.05 μm or smaller and a range of from 0.2 to 10 μm .
However, the former peak is caused by the spaces among
20 primary particles, while the latter peak is defined by the



1 spaces among secondary, tertiary or higher-order particles
aggregated by the primary particles. Therefore, this
sheet is different from the recording medium according to
the second aspect of the present invention, in which said
5 at least two peaks are caused by the spaces among primary
particles. Accordingly, the positions of the peaks of the
pore radii are quite different from those of the second
aspect of the present invention.

In the recording medium according to the second
10 aspect of the present invention, the ink-receiving layer
also has at least two peaks in the pore radius
distribution. The solvent component in an ink is absorbed
by relatively large pores, while the dye in the ink is
adsorbed by relatively small pores. The pore radius
15 corresponding to one of the peaks is preferably smaller
than 100 Å, more preferably 10 to 60 Å. The pore
radius corresponding to another peak is preferably within
a range of from 100 to 200 Å. If the pore radius
corresponding to the former peak is larger than the above
20 limit, the resulting recording medium is deteriorated in
the adsorption and fixing of the dye in the ink, and so
bleeding and beading occur on images. If the pore radius
corresponding to the latter peak is smaller than the lower
limit of the above range, the resulting recording medium
25 is deteriorated in the absorption of the solvent component
in the ink, so that the ink is not well dried, and the

1 surface of the ink-receiving layer remains wet even when
the medium is discharged out of a printer after printing.
If the pore radius corresponding to the latter peak is
greater than the upper limit of the above range, the
5 resulting ink-receiving layer tends to crack.

In the second aspect of the present invention, the
alumina hydrate also has at least two peaks in the pore
radius distribution. As with the ink-receiving layer, in
the pore radius distribution, the pore radius
10 corresponding to one of relatively small peaks is
preferably smaller than 100 Å, more preferably 10 to 60 Å.
The pore radius corresponding to a relatively large peak
is preferably within a range of from 100 to 200 Å. As
described above, the pore structure is defined by the
15 primary particles of the alumina hydrate. The nature of
this pore structure is already created by the alumina
hydrate. Therefore, if the pore radii corresponding to
the peaks of the pore radius distribution of the alumina
hydrate are outside the above ranges, the pore radii
20 corresponding to the peaks of the pore radius distribution
of the ink-receiving layer cannot be controlled within the
above range.

In the second aspect, the pore volume of the ink-
receiving layer is preferably within a range of from 0.1
25 to 1.0 cc/g, more preferably from 0.4 to 0.6 cc/g. If the
pore volume of the ink-receiving layer is greater than the

1 upper limit of the above range, cracking and dusting occur
on the ink-receiving layer. If the pore volume is smaller
than the lower limit of the above range, the resulting
recording medium is deteriorated in ink absorption. The
5 total pore volume of the ink-receiving layer is more
preferably at least 8 cc/m². If the total pore volume is
smaller than this limit, inks tend to run out of the ink-
receiving layer when multi-color printing is conducted,
and so bleeding occurs on images. The pore volume of
10 pores having a peak at a pore radius of smaller than 100 Å
is preferably within a range of from 0.1 to 10 % by
volume, more preferably from 1 to 5 % by volume based on
the total pore volume.

The pore volume of the pores having the peak at a
15 pore radius of smaller than 100 Å means a pore volume
within a range showing a breadth of pore radii having a
magnitude half of the greatest-magnitude pore radius of
the pores having a peak at smaller than 100 Å in the
pore radius distribution. If the pore volume of the pores
20 having a peak at a pore radius of smaller than 100 Å in
the ink-receiving layer is smaller than the lower limit of
the above range, the resulting recording medium is
deteriorated in adsorption of a dye in an ink. If the
pore volume exceeds the upper limit of the above range,
25 the resulting recording medium is deteriorated in the
absorption of the solvent component in the ink. The pore

1 volume of the alumina hydrate is also preferably within a
range of from 0.1 to 1.0 cc/g, more preferably from 0.4 to
0.6 cc/g. The pore volume of pores having a peak at a
pore radius of smaller than 100 Å is preferably within a
5 range of from 0.1 to 10 % by volume, more preferably from
1 to 5 % by volume based on the total pore volume. The
pore volume of the ink-receiving layer depends upon the
pore volume of the alumina hydrate. Therefore, if the
pore volume of the alumina hydrate is outside the above
10 range, the pore volume of the ink-receiving layer cannot
be controlled within the above range.

In the third aspect of the present invention, the
titanium dioxide-containing alumina hydrate is wide in the
half breadth of pore radius distribution as described
15 below. Such an alumina hydrate is dispersed up to a level
of primary particles in a dispersion for coating. Such
wide pore radius distribution is substantially kept even
after the formation of the ink-receiving layer through
steps of dispersion of the alumina hydrate, coating on the
20 base material and drying. The reason of this is not
clearly understood, but is considered to be as described
above.

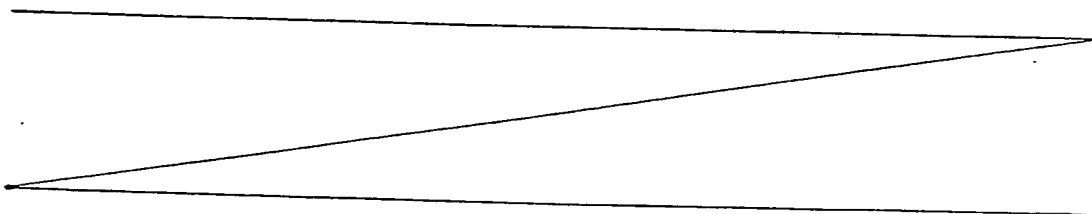
The average pore radius of the ink-receiving layer
is preferably within a range of from 20 to 200 Å, while
25 its half breadth of pore radius distribution is preferably
within a range of from 20 to 150 Å, more preferably from

1 80 to 150 Å.

If the average pore radius is larger than the upper limit of the above range, the resulting recording medium is deteriorated in the adsorption and fixing of a dye in an ink, and so bleeding tends to occur on images. If the average pore radius is smaller than the lower limit of the above range, the resulting recording medium is deteriorated in ink absorptiveness, and so beading tends to occur. On the other hand, if the half breadth is outside of this range, the resulting medium is deteriorated in the adsorption of a dye or a solvent system. As with the ink-receiving layer, the pore radius distribution of the alumina hydrate preferably has an average pore radius of 20 to 200 Å and a half breadth of pore radius distribution of 20 to 150 Å. The pore radius distribution of the ink-receiving layer depends upon the pore radius distribution of the alumina hydrate. Therefore, if the pore radius distribution of the alumina hydrate is outside the above range, the pore radius distribution of the ink-receiving layer cannot be controlled within the above range.

The pore volume of the ink-receiving layer is

25



1 preferably within a range of from 0.4 to 0.6 cc/g. If the
pore volume of the ink-receiving layer is greater than the
upper limit of the above range, cracking and dusting occur
on the ink-receiving layer. If the pore volume is smaller
5 than the lower limit of the above range, the resulting
recording medium is deteriorated in ink absorption. The
total pore volume of the ink-receiving layer is more
preferably at least 8 cc/m². If the total pore volume is
smaller than this limit, inks tend to run out of the ink-
10 receiving layer when multi-color printing is conducted,
and so bleeding occurs on images. As with the ink-
receiving layer, the pore volume of the alumina hydrate is
preferably within a range of from 0.4 to 0.6 cc/g. If the
pore volume of the alumina hydrate is outside the above
15 range, the pore volume of the ink-receiving layer cannot
be controlled within the above range.

In the preferred embodiment, the titanium dioxide-
containing alumina hydrate has at least two peaks in the
pore radius distribution. The alumina hydrate is
20 dispersed up to a level of primary particles in a
dispersion for coating. The pore radius distribution
having at least two peaks is not lost at all even when the
ink-receiving layer is formed therefrom. Such pore
structure as described above is defined principally by
25 spaces among the primary particles of the alumina hydrate.
The reason why the pore radius distribution has at least

1 two peaks is considered to be as described above. As
described above, pores corresponding to said at least two
peaks in the pore radius distribution are all caused by
the spaces among the primary particles. At least one of
5 the pore radii at one peak becomes smaller than the minor
axis or major axis radius of the flat plate surface of the
primary particles, while at least one of the pore radii at
another peak becomes about several times the minor axis or
major axis radius of the flat plate surface.

10 In the third aspect of the present invention, the
ink-receiving layer also has at least two peaks in the
pore radius distribution. The solvent component in an ink
is absorbed by relatively large pores, while the dye in
the ink is adsorbed by relatively small pores. The pore
15 radius corresponding to one of relatively small peaks is
preferably smaller than 100 \AA , with 10 to 60 \AA being
more preferred because the dye-adsorbing ability is
markedly improved. The pore radius corresponding to a
relatively large peak is preferably within a range of from
20 100 to 200 \AA because the rate of absorption of the
solvent becomes fast. If the pore radius corresponding to
the relatively small peak is larger than the above limit,
the resulting recording medium is deteriorated in the
adsorption and fixing of the dye in the ink, and so
25 bleeding and beading occur on images. If the pore radius
corresponding to the relatively large peak is smaller than

1 the lower limit of the above range, the resulting
recording medium is deteriorated in the absorption of the
solvent component in the ink, so that the ink is not well
dried, and the surface of the ink-receiving layer remains
5 wet even when the medium is discharged out of a printer
after printing. If the pore radius corresponding to the
latter peak is greater than the upper limit of the above
range, the resulting ink-receiving layer tends to crack.

In the third aspect of the present invention, the
10 alumina hydrate also has at least two peaks in the pore
radius distribution. As with the ink-receiving layer, in
the pore radius distribution, the pore radius
corresponding to one of relatively small peaks is
preferably smaller than 100 Å, more preferably 10 to 60 Å.
15 The pore radius corresponding to a relatively large peak
is preferably within a range of from 100 to 200 Å. As
described above, the pore structure is defined by the
primary particles of the alumina hydrate. The nature of
this pore structure is already created by the alumina
20 hydrate. Therefore, if the pore radii corresponding to
the peaks of the pore radius distribution of the alumina
hydrate are outside the above ranges, the pore radii
corresponding to the peaks of the pore radius distribution
of the ink-receiving layer cannot be controlled within the
25 above range.

In the third aspect, the pore volume of the ink-

1 receiving layer is preferably within a range of from 0.1
to 1.0 cc/g, more preferably from 0.4 to 0.6 cc/g. If the
pore volume of the ink-receiving layer is greater than the
upper limit of the above range, cracking and dusting occur
5 on the ink-receiving layer. If the pore volume is smaller
than the lower limit of the above range, the resulting
recording medium is deteriorated in ink absorption. The
total pore volume of the ink-receiving layer is more
preferably at least 8 cc/m². If the total pore volume is
10 smaller than this limit, inks tend to run out of the ink-
receiving layer when multi-color printing is conducted,
and so bleeding occurs on images. The pore volume of
pores having a peak at a pore radius of smaller than 100 Å
is preferably within a range of from 0.1 to 10 % by
15 volume, more preferably from 1 to 5 % by volume based on
the total pore volume.

As with the ink-receiving layer, the pore volume of
the alumina hydrate is also preferably within a range of
from 0.1 to 1.0 cc/g, more preferably from 0.4 to 0.6
20 cc/g. Further, the pore volume of pores having a peak at
a pore radius of smaller than 100 Å is preferably within
a range of from 0.1 to 10 % by volume, more preferably
from 1 to 5 % by volume based on the total pore volume.
The pore volume of the ink-receiving layer depends upon
25 the pore volume of the alumina hydrate. Therefore, if the
pore volume of the alumina hydrate is outside the above

1 range, the pore volume of the ink-receiving layer cannot
be controlled within the above range.

In the recording media according to the first to
third aspect of the present invention, which each have an
5 ink-receiving layer on a base material, a relative
pressure difference (ΔP) between adsorption and
desorption at 90 percent of the maximum amount of adsorbed
gas as found from an isothermal nitrogen adsorption and
desorption curve for the ink-receiving layer, which is
10 derived from the nitrogen adsorption and desorption
method, is preferably not larger than 0.2, more preferably
not larger than 0.15, most preferably not larger than
0.10. As described in McBain [J. Am. Chem. Soc., Vol. 57,
699 (1935)], the relative pressure difference (ΔP) can be
15 used as an index whether a pore in the form of an inkpot
may exist. The pore is closer to a straight tube as the
relative pressure difference (ΔP) is smaller. On the
other hand, the pore is closer to an inkpot as the
difference is greater. Differences exceeding the above
20 limit result in a recording medium poor in dryness of an
ink after printing. Japanese Patent Application Laid-Open
No. 60-245588 describes the fact that with respect to the
shape of pores in an alumina xerogel used in an ink-
receiving layer, those low in degree of labyrinth, even
25 and linear are preferred, while an inkpot form narrow in
inlet, a gourd form constricted in the middle and a

1 winding form are not preferred from the viewpoint of rate
of absorption. However, this publication does not
disclose anything about specific methods for measuring
actual physical properties and the like.

5 With respect to the above-described alumina hydrates
in the recording media according to the first to third
aspect of the present invention, a relative pressure
difference (ΔP) between adsorption and desorption at 90
percent of the maximum amount of adsorbed gas as found
10 from an isothermal nitrogen adsorption and desorption
curve for each of the alumina hydrates, which is derived
from the nitrogen adsorption and desorption method, is
preferably not larger than 0.2, more preferably not larger
than 0.15, most preferably not larger than 0.10. If the
15 difference is outside this limit, the relative pressure
difference (ΔP) of the ink-receiving layer as found from
the isothermal nitrogen adsorption and desorption curve
cannot be controlled within the above limit.

In the recording media according to the first to
20 third aspect of the present invention, the number of
hydroxyl groups on the surface of each of the alumina
hydrates is preferably at least 10^{20} groups/g. If the
number is fewer than this value, the solids concentration
of a dispersion in which the alumina hydrate is dispersed
25 in water cannot be increased. Such number of hydroxyl
groups on the surface of the alumina hydrate can be

1 determined by the titration with a triethylaluminum
solution.

The surface potential of each of the alumina
hydrates used in the present invention can be determined
5 by a zeta potential analyzer. Japanese Patent Application
Laid-Open No. 60-232990 discloses that alumina compounds
have a positive charge, and in its Examples, the values of
zeta-potentials. However, specific measuring method and
conditions are not described therein. The value of a
10 zeta-potential varies depending upon the cell and
electrode structure in a measuring apparatus, applied
voltage, the solids concentration and pH of a dispersion,
and dispersants and additives used. Therefore, absolute
values cannot be directly compared unless the measuring
15 conditions, apparatus and the like are standardized to
conduct the measurement.

With respect to the alumina hydrates used in the
present invention, the zeta-potential is preferably at
least 15 mV as measured at pH 6 in the form of a 0.1 % by
20 weight aqueous dispersion free from any dispersant and
additive. If the zeta-potential is above this limit, the
alumina hydrate can be easily dispersed up to a level of
primary particles in a dispersion. If the zeta-potential
is lower than 15 mV, aggregate and deposit occur as the
25 solids concentration increases, or particles partly
aggregate to form great lumps when a binder dispersion is

1 mixed with the alumina hydrate. For this reason, in
particular, in the recording media having an ink-receiving
layer, pore radius of the ink-receiving layer becomes
markedly large, and so the strength of the ink-receiving
5 layer is lowered, resulting in a potential problem that
dusting may occur, or dye-fixing ability upon printing may
be deteriorated. In general, alumina hydrate is stable in
a low pH region. It is therefore known to add an acid to
low the pH of the dispersion. However, the addition of
10 the acid is not preferred from the viewpoint of the
occurrence of offensive odor and corrosion and of the
limitation of the kind of binder used. Further, a known
process in which a dispersant is added is not preferred
because repellent or the like occurs upon the coating of
15 the dispersion.

On the other hand, if the pH region becomes higher,
primary particles aggregate according to the kind of the
alumina hydrate to enlarge the particle size, so that the
alumina hydrate may apparently have a high zeta-potential
20 in some cases. The zeta-potential recited in the present
invention should be measured in a condition that such
aggregation of particles does not occur. In order to
determine whether such aggregation of particles occurs or
not, it is effective to measure the particle size of
25 dispersed particles. Any known method may be used as a
measuring method of the particle size. It is

1 necessary to confirm that the particle size of particles
in a dispersion kept at pH 6, which is subjected to the
measurement of zeta-potential, has substantially the same
value as the particle size of particles in a dispersion
5 kept at pH 4 in which the particles are said to be stably
dispersed.

In the present invention, a dispersion obtained by
dispersing an alumina hydrate containing 0.1 to 1.0 % by
weight of a nitrate anion, said alumina hydrate being such
10 a specific alumina hydrate as described above, in
deionized water to give a solids concentration of 15 % by
weight preferably has a viscosity of not higher than 75
cP, most preferably not higher than 30 cP as measured at
20°C and a shear rate of 7.9 sec^{-1} . Further, a dispersion
15 obtained by dispersing the same alumina hydrate containing
0.1 to 1.0 % by weight of a nitrate anion as described
above in deionized water to give a solids concentration of
20 % by weight preferably has a viscosity of not higher
than 100 cP, most preferably not higher than 80 cP as
20 measured at 20°C and a shear rate of 10.2 sec^{-1} .

Furthermore, a dispersion obtained by dispersing the same
alumina hydrate containing 0.1 to 1.0 % by weight of a
nitrate anion as described above in deionized water to
give a solids concentration of 25 % by weight preferably
25 has a viscosity of not higher than 500 cP, most preferably
not higher than 460 cP as measured at 20°C and a shear

1 rate of 10.2 sec^{-1} . In each of the above cases, if the
viscosity exceeds the upper limit, the dispersion is
required to low its solids concentration. It is not hence
preferable from the viewpoint of mass productivity to
5 increase the viscosity beyond the above limit.

The viscosities of the alumina hydrate dispersions
according to the present invention can be measured by
means of a rotational viscometer, for example, a
Brookfield type viscometer.

10 The prior art making use of the pseudoboehmite cited
above and the present invention have been investigated in
comparison with each other. As a result, differences
therebetween are as follows:

1) With respect to the pore radius distribution in
15 the prior art, the breadth of the pore radius distribution
is disclosed only in a narrow range as demonstrated by the
fact that the pore volume of pores within a range of the
average pore radius $\pm 10 \text{ \AA}$ amounts to 45 to 55 % of the
total pore volume. On the contrary, the present inventor
20 has found that when the breadth of the pore radius
distribution is widened as described herein, print quality
remains unchanged even if the proportion of a dye to a
solvent in an ink and the composition of materials are
changed.

25 It has also been found that when one gets the pore
radius distribution to have at least two peaks to divide

1 the function of the pores, the solvent component in an ink
is absorbed in pores having a relatively large radius,
while the dye component in the ink is adsorbed on pores
having a relatively small radius, whereby a recording
5 medium, by which inks are quickly dried and good coloring
is achieved even when a multi-color printing is conducted
at high speed, is provided.

2) With respect to the pore radius and pore volume,
the prior art describes the total pore volumes as being
10 0.2 to 1.0 cc/g for pores having a pore radius of 10 to 40
Å, 0.1 to 0.4 cc/g for pores having a pore radius of 40 to
100 Å, and 0.1 cc/g for pores having a pore radius of 100
to 1000 Å. On the contrary, the present inventor has
found that when the relationship between the pore volume
15 per unit area of the ink-receiving layer and the
isothermal nitrogen adsorption and desorption curve
thereof is adjusted within the range described herein, the
adsorption and drying of the ink after printing are
markedly improved.

20 3) The prior art describes a pseudoboehmite sol in
the form of a needle and a production process of an ink-
receiving layer making use of the sol. The shape of the
alumina hydrate and the solids concentration of a
dispersion are also described. On the contrary, the
25 present inventor has found the use of non-crystal alumina
hydrates in the form of "a flat plate".

1 As described above, such a non-crystal alumina
hydrate in the form of a flat plate is produced by
hydrolyzing an aluminum long-chain alkoxide. Therefore,
it is possible to obtain an alumina hydrate containing
5 little ion and raw alcohol with ease. According to this
hydrolysis, the shape control for forming particles of the
alumina hydrate into the flat plate can be made with ease.
The non-crystal alumina hydrate in the flat plate form has
higher dispersibility than the known alumina hydrate in
10 the needle form. Further, the resulting alumina hydrate
is dried once to powder without directly preparing a
dispersion in a sol state, and then used, whereby a
dispersion high in solids concentration and low in
viscosity can be prepared with ease.

15 4) The prior art discloses an alumina hydrate of a
pseudoboehmite structure. It is also disclosed to add
additives such as silica, boria, titania and magnesia to
the alumina hydrate. On the contrary, the present
inventor has found that an alumina hydrate containing
20 titanium dioxide has an improving effect on both
adsorption of a dye in an ink and dispersibility.

The titanium dioxide-containing alumina hydrate is
better in dye-adsorbing ability than alumina hydrate
containing no titanium dioxide because the dye is adsorbed
25 on the strongly electron-acceptable Al^{3+} formed by the
action of titanium dioxide, or the titanium ion of

1 titanium dioxide forms a coordinate bond with the dye.
Figs. 9A and 9B schematically illustrate exposed states of
titanium dioxide in pores in the respective cases where
titanium dioxide is internally contained in the alumina
5 hydrate and where titanium dioxide is added (mixed) to the
alumina hydrate. In the mixed system, the titanium
dioxide is partly exposed in the pore. In the contained
system, the titanium dioxide is entirely exposed in the
pore. If the titanium dioxide is present in the same
10 proportion, the system according to the present invention
is greater on the amount of titanium dioxide exposed.

In the titanium dioxide-containing alumina hydrate
used in the present invention, the titanium dioxide exists
in the close vicinity of the surface of the alumina
15 hydrate in the form of such ultrafine particles that they
cannot be observed even through an electron microscope.
Therefore, the surface area of the titanium dioxide in the
interior of the pore is considerably great, and an
adsorption site hence becomes far greater than the mixed
20 system, whereby the adsorptiveness of a dye in an ink to
the alumina hydrate is exhibited to a significant extent.

In the alumina hydrate mixed with titanium dioxide,
its surface charge tends to be lost because the surface
charges of the alumina hydrate and titanium dioxide are
25 opposite to each other, and hence neutralized. Therefore,
the zeta-potential of its dispersion is low, and so the

1 dispersion tends to aggregate. On the contrary, in the
titanium dioxide-containing alumina hydrate used in the
present invention, the titanium dioxide exists in the
close vicinity of the surface of the alumina hydrate in
5 the form of the ultrafine particles, whereby the surface
area of the titanium dioxide in the interior of the pore
is considerably great, and little influence is exerted on
the structure of the alumina hydrate. It also has an
effect of lessening the reduction in surface charge of the
10 alumina hydrate. Further, in the present invention, the
titanium dioxide exists only in the vicinity of the
surface of the alumina hydrate. Therefore, the bulk
properties of the interior of the alumina hydrate are easy
to be kept, which has an effect of exerting little
15 influence on the surface charge.

The prior art describes a psuedoboehmite sol and a
production process of an ink-receiving layer making use of
the sol. On the contrary, the non-crystal titanium
dioxide-containing alumina hydrates in the form of a flat
20 plate according to the present invention is produced by
hydrolyzing, preferably, an aluminum long-chain alkoxide
and titanium alkoxide. Therefore, it is possible to
obtain an alumina hydrate containing little ion and raw
alcohol with ease. According to this process, the alumina
25 hydrate tend to become particles in the form of a flat
plate, and shape control can be made with ease. Further,

1 titanium dioxide exists in the close vicinity of the
surfaces of the particles, so that the alumina hydrate has
far higher dispersibility than the known alumina hydrate
in the needle form. Furthermore, the resulting titanium
5 dioxide-containing alumina hydrate is dried once to powder
without directly preparing a dispersion (in particular, a
dispersion for coating) in a sol state, and then used,
whereby a dispersion high in solids concentration and low
in viscosity can be prepared with ease.

10 In each of the recording media according to the
present invention, a binder capable of using in
combination with the alumina hydrate may be freely
selected from water-soluble polymers. For example,
preference may be given to polyvinyl alcohol or modified
15 products thereof (cationically modified, anionically
modified, silanol modified), starch or modified products
thereof (oxidized, etherified), casein or modified
products thereof, gum arabic, cellulose derivatives such
as carboxymethyl cellulose, hydroxyethyl cellulose and
20 hydroxypropylmethyl cellulose, conjugated diene copolymer
latexes such as SBR latexes, NBR latexes and methyl
methacrylate-butadiene copolymers, functional group-
modified polymer latexes, vinyl copolymer latexes such as
ethylene-vinyl acetate copolymers, polyvinyl pyrrolidone,
25 maleic anhydride polymer or copolymers thereof, acrylic
ester copolymers, and the like. These binders may be used

1 either singly or in any combination thereof. The mixing
ratio of the alumina hydrate to the binder may be
optionally selected from a range of from 1:1 to 30:1,
preferably from 5:1 to 25:1. If the amount of the binder
5 is less than the lower limit of the above range, the
mechanical strength of the resulting ink-receiving layer
is insufficient, which forms the cause of cracking and
dusting. If the amount is greater than the upper limit of
the above range, the pore volume of the resulting ink-
10 receiving layer is reduced, resulting in a recording
medium poor in ink absorptiveness.

The alumina hydrate and binder may optionally
contain dispersants for the alumina hydrate, viscosity
modifiers, pH adjustors, lubricants, flowability
15 modifiers, surfactants, antifoaming agents, water-
proofings, foam suppressors, releasing agents, foaming
agents, penetrants, coloring dyes, optical whitening
agents, ultraviolet absorbents, antioxidants, antiseptics
and mildewproofing agents.

20 The water-proofings may be freely selected for use
from the known substances such as quaternary ammonium
halides and quaternary ammonium salt polymers.

As the base material constituting the recording
medium of the present invention, may be used paper webs
25 such as suitably sized paper, water leaf paper and resin-
coated paper making use of polyethylene or the like,

1 sheet-like substance such as thermoplastic films, and
cloths. No particular limitation is imposed on the base
material. In the case of the thermoplastic films, may be
used transparent films such as films of polyester,
5 polystyrene, polyvinyl chloride, polymethyl methacrylate,
cellulose acetate, polyethylene and polycarbonate, as well
as opaque sheets opacified by the filling of an alumina
hydrate or the formation of minute foams.

A dispersion of the alumina hydrate, which is
10 suitably used in the production of the recording medium
according to the present invention, can be prepared in the
following manner. The above-described powdery alumina
hydrate is added to deionized water to prepare a
dispersion containing solids at a desired concentration.
15 Mechanical shear force or ultrasonic energy is applied to
the dispersion, as needed, to control the particle size of
the alumina hydrate. Thereafter, a binder dispersion
separately prepared is added to the former dispersion.
The resulting mixture is subjected to dispersion, heating,
20 defoaming and/or the like as needed, thereby obtaining a
final dispersion for coating.

In the recording media having an ink-receiving layer
according to the present invention, as a process for
forming the ink-receiving layer on the base material, may
25 be used a process in which the dispersion containing the
alumina hydrate and the like is applied to the base

1 material by means of a coater, and then dried. As a
coating process, may be used a generally-used coating
technique making use of a blade coater, air knife coater,
roll coater, brush coater, curtain coater, bar coater,
5 gravure coater or sprayer. The coating weight of the
dispersion is within a range of from 0.5 to 60 g/m², more
preferably from 5 to 45 g/m² in dried state. As needed,
the resulting recording medium may be subjected to
supercalendering or the like so as to improve the
10 smoothness of the ink-receiving layer.

The recording media of another type according to the
present invention, in which the alumina hydrate is
internally contained in the base material, can be produced
using an internally-adding process in which the alumina
15 hydrate (its dispersion) is added to a slurry containing a
fibrous material in a paper making process. In such an
internally-adding process, a paper-strength improving
agent, retention aid and colorant may be added for use as
needed. The retention aid may be selected from cationic
20 retention aids such as cationic starch and dicyanedi-
amides, formalin condensates, and anionic retention aids such as
anionic polyacrylamide and anionic colloidal silica.
These may also be used in combination with each other.

Inks used in conducting recording on the recording
25 media according to the present invention comprises
principally a coloring material (dye or pigment), a water-

1 soluble organic solvent and water. Preferred examples of
the coloring material include water-soluble dyes
represented by direct dyes, acid dyes, basic dyes,
reactive dyes and food colors. However, any coloring
5 materials may be used so far as they provide images
satisfying required performance such as fixing ability,
coloring ability, brightness, stability, light fastness
and the like in combination with the above-described
recording media.

10 The water-soluble dyes are generally used by
dissolving them in water or a solvent composed of water
and at least one organic solvent. As a preferable solvent
component for these dyes, may be used a mixed solvent
composed of water and at least one of various water-
15 soluble organic solvents. It is however preferable to
control the content of water in an ink within a range of
from 20 to 90 % by weight, more preferably from 60 to 90 %
by weight.

Examples of the water-soluble organic solvents
20 include alkyl alcohols having 1 to 4 carbon atoms, such as
methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl
alcohol, n-butyl alcohol, sec-butyl alcohol, tert-butyl
alcohol and isobutyl alcohol; amides such as
dimethylformamide and dimethylacetamide; ketones and keto
25 alcohols such as acetone and diacetone alcohol; ethers
such as tetrahydrofuran and dioxane; polyalkylene glycols

1 such as polyethylene glycol and polypropylene glycol;
alkylene glycols the alkylene moiety of which has 2 to 6
carbon atoms, such as ethylene glycol, propylene glycol,
hexylene glycol and diethylene glycol; thiodiglycol;
5 1,2,6-hexanetriol; glycerol; lower alkyl ethers of
polyhydric alcohols, such as ethylene glycol methyl ether,
diethylene glycol methyl ether, diethylene glycol ethyl
ether, triethylene glycol monomethyl ether and triethylene
glycol monoethyl ether; and the like. Among these many
10 water-soluble organic solvents, the polyhydric alcohols
such as diethylene glycol, and the lower alkyl ethers of
polyhydric alcohol, such as triethylene glycol monomethyl
ether and triethylene glycol monoethyl ether are
preferred. The polyhydric alcohols are particularly
15 preferred because they have an effect as a lubricant for
inhibiting the clogging of nozzles, which is caused by the
evaporation of water in an ink and hence the deposition of
a water-soluble dye.

A solubilizer may be added to the inks. Nitrogen-
20 containing heterocyclic ketones are typical solubilizers.
Its object is to enhance the solubility of the water-
soluble dye in the solvent by leaps and bounds. For
example, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-
imidazolidinone are preferably used. In order to further
25 improve the properties of inks, may be added additives
such as viscosity modifiers, surfactants, surface tension

1 modifiers, pH adjustors and specific resistance adjustors.

A preferred method of conducting recording by
applying the above-described ink to the recording medium
is an ink-jet recording method. As such a method, any
5 systems may be used so far as they can effectively eject
an ink out of a nozzle to apply it to the recording
medium. In particular, an ink-jet recording system
described in Japanese Patent Application Laid-Open No. 54-
59936, in which an ink undergoes a rapid volumetric change
10 by an action of thermal energy applied to the ink, so that
the ink is ejected out of a nozzle by the working force
generated by this change of state, may be used
effectively.

[Examples]

15 The present invention will hereinafter be described
more specifically by the following Examples. However, the
present invention is not limited to these examples. The
measurements of various properties according to this
invention were conducted with the following points in
20 mind:

- 1) BET specific surface area, pore radius distribution,
pore volume and isothermal adsorption and desorption
curve:

After an alumina hydrate sample or a recording
25 medium sample in which an ink-receiving layer had been
formed on a PET film was thoroughly heated and deaerated,

1 measurement was conducted using the nitrogen adsorption
and desorption method (Autosorb 1, manufactured by
Quanthachrome Co.).

i) The BET specific surface area was calculated in
5 accordance with the method of Brunauer, et al. [J. Am.
Chem. Soc., Vol. 60, 309 (1938)].

ii) The pore radius and pore volume were calculated
in accordance with the method of Barrett, et al. [J. Am.
Chem. Soc., Vol. 73, 373 (1951)].

10 iii) The relative pressure difference (ΔP) between
adsorption and desorption at 90 percent of the maximum
amount of adsorbed gas was found from an isothermal
nitrogen adsorption and desorption curve.

2) X-ray diffraction pattern:

15 An X-ray diffractometer (manufactured by RIGAKU
CORPORATION) was used.

3) Shape observation of alumina hydrate (aspect ratio and
slenderness ratio):

An alumina hydrate sample was dispersed in deionized
20 water, and the resultant dispersion was dropped on a
collodion membrane to prepare a sample for measurement.
This sample was observed through a transmission type
electron microscope (H-500, manufactured by Hitachi Ltd.).

4) Number of hydroxyl groups:

25 One gram of an alumina hydrate sample was weighed
out to titrate it with triethylaluminum.

1 5) Zeta-potential:

An alumina hydrate sample was dispersed in deionized water to give a solids concentration of 0.1 % by weight, and the dispersion was then adjusted to pH 6 with a nitric acid, thereby conducting measurement. (Bi-ZETA plus, manufactured by Brookhaven Co., dispersion temperature: 20°C, an acrylic cell was used.)

6) Solution viscosity:

10 An aqueous dispersion sample at solids concentration of 15 % by weight, 20 % by weight or 25 % by weight was prepared to measure its viscosity at 20°C and a shear rate of 7.9 sec^{-1} (in the case of the solids concentration of 15 % by weight) or 10.9 sec^{-1} (in the case of the solids concentration of 20 % by weight or 25 % by weight) by
15 means of a VISCOMETER manufactured by TOKIMEC Co.

7) Nitrate anion:

A nitrate anion was extracted from an alumina hydrate sample with hot water to measure its quantity by an ion-exchange chromatograph (L-3720, manufactured by
20 Hitachi Ltd.), thereby determining the quantity of the nitrate anion in terms of % by weight of dried alumina hydrate.

8) Quantitative analysis of titanium dioxide:

The content of titanium dioxide in the whole alumina
25 hydrate sample was determined by fusing the alumina hydrate sample in a borate in accordance with the ICP

1 method (SPS 4000, manufactured by Seiko-Electronic Inc.).
The distribution of titanium dioxide in the alumina
hydrate sample was analyzed by means of an ESCA (Model
2803, manufactured by Surface Science Instruments Co.).
5 The surface of the alumina hydrate sample was etched with
an argon ion for 100 seconds and 500 seconds to determine
the change in content of the titanium dioxide. Etching
conditions was as follows:

Argon pressure: 5×10^{-4} Pa

10 Voltage applied: 3 kV

Current (d.c.) applied: 3 mA.

[First aspect]

Examples 1 to 4:

Aluminum dodeoxide was prepared in accordance with
15 the process described in U.S. Patent No. 4,242,271. The
aluminum dodeoxide was then hydrolyzed in accordance with
the process described in U.S. Patent No. 4,202,870 to
prepare an alumina slurry. Water was added to the alumina
slurry until the solid content of alumina hydrate was 7.9
20 %. The pH of the alumina slurry was 9.5. A 3.9 % nitric
acid solution was added to adjust the pH of the slurry.
Colloidal sols were obtained under their corresponding
aging conditions shown in Table 1. Each of these
colloidal sols was spray-dried at 75°C to obtain its
25 corresponding alumina hydrate. This alumina hydrate was
non-crystal as shown by an X-ray diffraction pattern in

1 Fig. 2. As illustrated by a photograph (an electron
microphotograph: 60,000 magnifications) in Fig. 3, it was
also in the form of a flat plate. The physical property
values of the resulting alumina hydrates were measured in
5 accordance with the respective methods described above.
The results are shown in Table 2 and Figs. 5 and 6.

Polyvinyl alcohol (Gohsenol NH18, product of The
Nippon Synthetic Chemical Industry Co., Ltd.) was
dissolved or dispersed in deionized water to obtain a 10 %
10 by weight solution or dispersion. The four different
kinds of alumina hydrates obtained above were separately
similarly dispersed in deionized water to obtain 15 % by
weight dispersions. Each of the alumina hydrate
dispersions and the polyvinyl alcohol solution were
15 weighed out to give a weight ratio of 10:1 in terms of
solids and mixed with each other. The resultant mixture
was stirred to obtain a mixed dispersion. The mixed
dispersion was applied by a die coating process to one
side of a PET film (Lumirror, product of Toray Industries,
20 Inc.) having a thickness of 100 μm to form an ink-
receiving layers having a thickness of 30 μm . Fig. 4 is a
photograph (an electron microphotograph: 50,000
magnifications) illustrating the section of the ink-
receiving layer and indicates that the alumina hydrate in
25 the form of a flat plate lies at random in the ink-
receiving layer. The physical property values of the ink-

1 receiving layer were measured in accordance with the
respective methods described above. The results are shown
in Table 3. Printing was conducted on the thus-obtained
recording media to evaluate their printability in
5 accordance with the following standards. The evaluation
results are also shown in Table 3.

Printability:

Using an ink-jet printer equipped with four
recording heads for yellow, magenta, cyan and black inks,
10 each of said heads having 128 nozzles in a proportion of
16 nozzles per mm, ink-jet recording was conducted with
inks of the following compositions, thereby evaluating the
recording media in ink-drying ability (absorptiveness),
optical density of an image, bleeding and beading.

15 (1) Ink-drying ability:

After single-color or multi-color solid printing was
conducted with the yellow, magenta, cyan and black inks of
the following ink composition 1, the recorded area of each
recording medium was touched with a finger to determine
20 the drying condition of the inks on the surface of the
recording medium. The quantity of ink in the single-color
printing was determined as 100 %. The ink-drying ability
was ranked as A where none of the inks adhered to the
finger in an ink quantity of 200 %, B where none of the
25 inks adhered to the finger in an ink quantity of 100 %, or
C where any ink adhered to the finger in an ink quantity

1 of 100 %.

(2) Optical density:

Solid printing was conducted separately with the yellow, magenta, cyan and black inks of the following ink composition 1. The optical density of each of the images formed was determined by means of a Macbeth reflection densitometer RD-918.

(3) Bleeding and beading:

After single-color or multi-color solid printing was conducted with the yellow, magenta, cyan and black inks of the following ink composition 1, the recording media were evaluated by whether bleeding occurred on their surfaces. Besides, single-color or multi-color solid printing was conducted with the respective yellow, magenta, cyan and black inks of the following two ink compositions to visually evaluate the recording media by whether beading occurred. The quantity of ink in the single-color printing was determined as 100 %. The resistance to bleeding or the resistance to beading of the recording media was ranked as A where bleeding or beading did not occur in an ink quantity of 200 %, B where bleeding or beading did not occur in an ink quantity of 100 %, or C where bleeding or beading occurred in an ink quantity of 100 %.

25 Ink composition 1:

Dye

5 parts

1	Diethylene glycol	10 parts
	Polyethylene glycol	10 parts
	Water	75 parts.

Ink composition 2:

5	Dye	5 parts
	Glycerol	15 parts
	Polyethylene glycol	20 parts
	Water	70 parts.

Dye in ink:

10	Yellow (Y): C.I. Direct Yellow 86
	Magenta (M): C.I. Acid Red 35
	Cyan (C): C.I. Direct Blue 199
	Black (Bk): C.I. Food Black 2.

Examples 5 to 8:

15 Each of the alumina hydrate dispersions prepared in
Examples 1 to 4 and the polyvinyl alcohol dispersion as
described in Examples 1 to 4 were weighed out to give a
weight ratio of 15:1 in terms of solids and mixed with
each other. The resultant mixture was stirred to obtain a
20 mixed dispersion. The mixed dispersion was applied by an
air knife coating process to one side of a wood free paper
web (Shiraoi 157, product of Daishowa Paper Manufacturing
Co., Ltd.) at a rate of 20 g/m² to form an ink-receiving
layer. Printing was conducted on the thus-obtained
25 recording media to evaluate their printability in
accordance with the above-described standards. The

1 evaluation results are shown in Table 4.

Examples 9 to 12:

A paper web having a basis weight of 70 g/m² was made by means of a TAPPI standard sheet former by using,
5 as raw pulp, 80 parts of bleached hardwood kraft pulp (LBKP) having a freeness (C.S.F.) of 370 ml and 20 parts of bleached softwood kraft pulp (NBKP) having a freeness of 410 ml, incorporating, as a filler, each of the alumina hydrates prepared in Examples 1 to 4 in a proportion of 35
10 % by weight based on the solid content of the pulp and as a retention aid, cationic starch (CATOF, product of Oji National K.K.) in a proportion of 0.3 % by weight based on the solid content of the pulp into the pulp, and then adding 0.05 % by weight of a polyacrylamide retention aid
15 (Pearlflock FR-X, product of Seiko Chemical Industries Co., Ltd.) right before paper making. A 2 % solution of oxidized starch (MS3800, product of Nihon Shokuhin Kako Co., Ltd.) was then applied to the web by a size press to obtain a recording media. Printing was conducted on the
20 thus-obtained recording media to evaluate their printability in accordance with the above-described standards. The evaluation results are shown in Table 5.

Comparative Example 1:

An alumina sol (AS-2, product of Catalyst & Chemical
25 Industries Co., Ltd.) and polyvinyl alcohol (PVA 117, product of Kuraray Co., Ltd.) were applied to the same PET

1 film as that used in Example 1 in accordance with the
process described in Example 1 of Japanese Patent
Application Laid-Open No. 4-4181 to prepare a recording
medium. The zeta-potential of the alumina sol was
5 measured in accordance with the method described above.
Further, the alumina sol was concentrated to a solids
concentration of 15 % to measure its viscosity. The
physical property values and evaluation results thereof
are shown in Table 6.

10 Comparative Example 2:

A recording medium was prepared by using an alumina
sol (AS-3, product of Catalyst & Chemical Industries Co.,
Ltd.) and the same polyvinyl alcohol as that used in
Comparative Example 1 in accordance with the process
15 described in Example 4 of Japanese Patent Application
Laid-Open No. 4-4181. The physical property values and
evaluation results thereof are shown in Table 6.

Comparative Example 3:

A recording medium was prepared by using an alumina
20 sol (100, product of Nissan Chemical Industries, Ltd.) and
the same polyvinyl alcohol as that used in Comparative
Example 1 in accordance with the process described in
Example 1 of Japanese Patent Application Laid-Open No. 3-
143678. The physical property values and evaluation
25 results thereof are shown in Table 6.

Comparative Example 4:

An alumina sol was prepared in accordance with the

1 process described in Example 1 of Japanese Patent
Application Laid-Open No. 5-32037. A recording medium was
prepared by using this alumina sol and the same polyvinyl
alcohol as that used in Comparative Example 1. The
5 physical property values and evaluation results thereof
are shown in Table 6.

Table 1

Aging condition	Sample			
	Ex. 1	Ex. 2	Ex. 3	Ex. 4
10 pH before aging	5.6	6.9	6.0	5.8
Aging temperature (°C)	110	150	180	120
Aging period (hrs)	8	4	3	5
Aging apparatus	Auto- clave	Auto- clave	Auto- clave	Auto- clave

15

20

25

Table 2

Item determined	Sample			
	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Average particle size (nm)	43	38	32	26
Aspect ratio	3.3	5.6	7.9	10.0
Slenderness ratio	0.7	0.7	0.7	0.7
BET specific surface area (m ² /g)	75	93	135	200
Average pore radius (Å)	125	85	50	30
Half breadth (Å)	100	80	50	20
Pore volume (cc/g)	0.57	0.55	0.55	0.51
Relative pressure difference (ΔP)	0.03	0.02	0.10	0.10
Number of OH groups (groups/g)	2.0x10 ²⁰	1.8x10 ²⁰	1.5x10 ²⁰	1.6x10 ²⁰
Zeta-potential (mV)	20	23	17	17
Nitrate anion (% by weight)	0.1	0.1	1.0	1.0
Dispersion viscosity				
15 % by weight	20	20	17	17
(cP) 20 % by weight	77	59	49	61
25 % by weight	409	460	430	457

1

Table 3

Item determined	Sample			
	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Average pore radius (Å)	125	80	40	30
Half breadth (Å)	140	100	60	40
Pore volume (cc/g)	0.53	0.50	0.50	0.49
(cc/m ²)	9.0	8.6	8.4	8.2
Relative pressure difference (ΔP)	0.03	0.07	0.02	0.10
Printability:				
Drying ability	A	A	A	A
Optical density: Y	1.58	1.55	1.53	1.53
M	1.47	1.50	1.48	1.52
C	1.60	1.57	1.61	1.55
Bk	1.64	1.61	1.59	1.57
Bleeding	A	A	A	A
Beading				
Ink composition 1	A	A	A	A
Ink composition 2	A	A	A	A

15

Table 4

Item determined	Sample			
	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Printability:				
Drying ability	A	A	A	A
Optical density: Y	1.42	1.42	1.44	1.43
M	1.43	1.47	1.46	1.45
C	1.47	1.45	1.46	1.49
Bk	1.48	1.47	1.45	1.46
Bleeding	A	A	A	A
Beading				
Ink composition 1	A	A	A	A
Ink composition 2	A	A	A	A

25

Table 5

Item determined	Sample			
	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Printability:				
Drying ability	A	A	A	A
Optical density: Y	1.02	1.02	1.04	1.03
M	1.03	1.07	1.06	1.05
C	1.07	1.05	1.06	1.09
Bk	1.08	1.07	1.05	1.06
Bleeding	A	A	A	A
Beading				
Ink composition 1	A	A	A	A
Ink composition 2	A	A	A	A

Table 6

Item determined	Sample			
	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Zeta-potential (mV)	10	7	9	10
Dispersion viscosity (cP)	200	250	180	230
Average pore radius (Å)	20	33	20	60
Peak 1 of pore distribution (Å)	20	30	22	60
Peak 2 of pore distribution (Å)	---	---	---	---
Half breadth (Å)	10	14	12	15
Pore volume (cc/g) (cc/m ²)	0.83 1.0	0.50 0.8	0.06 0.01	0.66 2.0
Relative pressure difference (ΔP)	0.25	0.25	0.23	0.23
Printability:				
Drying ability	C	C	C	C
Optical density: Y	1.68	1.67	1.66	1.69
M	1.51	1.54	1.53	1.50
C	1.50	1.52	1.51	1.53
Bk	1.46	1.48	1.47	1.46
Bleeding	B	B	B	A
Beading				
Ink composition 1	B	B	B	A
Ink composition 2	C	B	C	B

1 [Second aspect]

Examples 13 to 16:

Alumina hydrates were obtained in the same manner as in Examples 1 to 4 except that the aging conditions in
5 Examples 1 to 4 were changed to aging conditions shown in Table 7.

These alumina hydrates showed an X-ray diffraction pattern similar to that illustrated in Fig. 2 and were hence amorphous. A photograph similar to the photograph
10 (an electron microphotograph: 60,000 magnifications) in Fig. 3 was taken, and it was hence confirmed that they were in the form of a flat plate. The physical property values of the alumina hydrates were measured in accordance with the respective methods described above. The results
15 are shown in Table 8 and Figs. 7 and 8.

Table 7

Aging condition	Sample			
	Ex. 13	Ex. 14	Ex. 15	Ex. 16
pH before aging	6.6	6.9	7.0	6.8
20 Aging temperature (°C)	30	45	50	50
Aging period	2 weeks	12 days	8 days	5 days
Aging apparatus	Oven	Oven	Oven	Auto-clave

Recording media comprising a PET film and an ink-
25 receiving layer provided on the PET film were obtained in the same manner as in Examples 1 to 4 except that these

1 alumina hydrates were respectively used.

The physical property values of the ink-receiving
layers of these recording media and the evaluation results
as to the printability of these recording media are shown
5 in Table 9.

The evaluation of the printability was conducted in
accordance with the following standards.

Printability:

Using an ink-jet printer equipped with four
10 recording heads for yellow, magenta, cyan and black inks,
each of said heads having 128 nozzles in a proportion of
16 nozzles per mm, ink-jet recording was conducted with
the inks of the ink composition 1 described in Examples 1
to 4, thereby evaluating the recording media in ink-drying
15 ability (absorptiveness), optical density of an image,
bleeding and beading.

(1) Ink-drying ability:

After single-color or multi-color solid printing was
conducted with the yellow, magenta, cyan and black inks,
20 the recorded area of each recording medium was touched
with a finger to determine the drying condition of the
inks on the surface of the recording medium. The quantity
of ink in the single-color printing was determined as 100
%. The ink-drying ability was ranked as AA where none of
25 the inks adhered to the finger in an ink quantity of 300
%, A where none of the inks adhered to the finger in an

1 ink quantity of 200 %, B where none of the inks adhered to
the finger in an ink quantity of 100 %, or C where any ink
adhered to the finger in an ink quantity of 100 %.

(2) Optical density:

5 Solid printing was conducted with the black ink.
The optical density of the image formed was determined by
means of a Macbeth reflection densitometer RD-918.

(3) Bleeding and beading:

After single-color or multi-color solid printing was
10 conducted with the yellow, magenta, cyan and black inks,
the recording media were visually evaluated by whether
bleeding or beading occurred on their surfaces. The
quantity of ink in the single-color printing was
determined as 100 %. The resistance to bleeding or the
15 resistance to beading of the recording media was ranked as
AA where bleeding or beading did not occur in an ink
quantity of 300 %, A where bleeding or beading did not
occur in an ink quantity of 200 %, B where bleeding or
beading did not occur in an ink quantity of 100 %, or C
20 where bleeding or beading occurred in an ink quantity of
100 %.

Table 8

Item determined	Sample			
	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Average particle size (nm)	40	35	31	28
Aspect ratio	3.8	5.8	7.6	9.8
Slenderness ratio	0.7	0.7	0.7	0.7
BET specific surface area (m ² /g)	80	95	130	190
Peak 1 of pore distribution (Å)	125	110	140	120
Peak 2 of pore distribution (Å)	17	30	50	60
Pore volume (cc/g)	0.57	0.55	0.55	0.51
Volume ratio of peak 2 (%)	5	8	10	10
Relative pressure difference (ΔP)	0.03	0.02	0.10	0.10
Number of OH groups (groups/g)	1.9x10 ²⁰	1.5x10 ²⁰	1.7x10 ²⁰	2.0x10 ²⁰
Zeta-potential (mV)	20	23	17	17
Nitrate anion (% by weight)	0.1	0.5	0.7	1.0
Dispersion viscosity				
15 % by weight	18	18	17	16
20 % by weight	43	50	80	75
25 % by weight	415	430	480	467

Table 9

Item determined	Sample			
	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Peak 1 of pore distribution (Å)	125	110	125	130
Peak 2 of pore distribution (Å)	25	30	40	60
Pore volume (cc/g)	0.53	0.50	0.50	0.49
(cc/m ²)	9.0	8.6	8.4	8.2
Relative pressure difference (ΔP)	0.03	0.07	0.02	0.10
Volume ratio of peak 2 (%)	5	8	10	10
Printability:				
Drying ability	AA	AA	AA	AA
Optical density	1.65	1.67	1.66	1.67
Bleeding	AA	AA	AA	AA
Beading	AA	AA	AA	AA

Examples 17 to 20:

Each of the alumina hydrate dispersions prepared in Examples 13 to 16 and the polyvinyl alcohol dispersion as described in Examples 1 to 4 were weighed out to give a weight ratio of 15:1 in terms of solids and mixed with each other. The resultant mixture was stirred to obtain a mixed dispersion. The mixed dispersion was applied by an air knife coating process to one side of a wood free paper web (Shiraoi 157, product of Daishowa Paper Manufacturing Co., Ltd.) at a rate of 20 g/m² to form an ink-receiving layer. Printing was conducted on the thus-obtained recording media to evaluate their printability in accordance with the above-described standards. The

1 evaluation results are shown in Table 10.

Table 10

Item determined	Sample			
	Ex. 17	Ex. 18	Ex. 19	Ex. 20
Printability:				
Drying ability	AA	AA	AA	AA
Optical density	1.51	1.52	1.51	1.52
Bleeding	AA	AA	AA	AA
Beading	AA	AA	AA	AA

10 Examples 21 to 24:

Recording media were obtained in the same manner as in Examples 9 to 12 except that the alumina hydrates prepared in Examples 13 to 16 were respectively used. Printing was conducted on the thus-obtained recording media to evaluate their printability in accordance with the above-described standards. The evaluation results are shown in Table 11.

Table 11

Item determined	Sample			
	Ex. 21	Ex. 22	Ex. 23	Ex. 24
Printability:				
Drying ability	AA	AA	AA	AA
Optical density	1.08	1.09	1.08	1.09
Bleeding	AA	AA	AA	AA
Beading	AA	AA	AA	AA

1 [Third aspect]

Examples 25 and 26:

Aluminum dodeoxide was prepared in accordance with the process described in U.S. Patent No. 4,242,271.

5 Isopropyltitanium (product of Kishida Chemical Co., Ltd.) was then mixed in an amount 5/1000 times of the weight of the aluminum dodeoxide. The resulting aluminum dodeoxide mixture was hydrolyzed in accordance with the process described in U.S. Patent No. 4,202,870 to prepare a
10 titanium dioxide-containing alumina slurry. Water was added to the alumina slurry until the solid content of alumina hydrate was 7.9 %. The pH of the alumina slurry was 9.5. A 3.9 % nitric acid solution was added to adjust the pH of the slurry. Colloidal sols were obtained under
15 their corresponding aging conditions shown in Table 13. Each of these colloidal sols was spray-dried to obtain its corresponding alumina hydrate. This alumina hydrate showed an X-ray diffraction pattern similar to that illustrated in Fig. 2 and was hence non-crystal. A
20 photograph similar to the photograph (an electron microphotograph: 60,000 magnifications) in Fig. 3 was taken, and it was hence confirmed that its form was a flat plate form. The surface of the alumina hydrate was observed through an FE-TEM (HF 2000, manufactured by
25 Hitachi Ltd.) of 500,000 magnifications. As a result, no titanium dioxide was observed. The physical property

1 values of the alumina hydrates were measured in accordance
with the respective methods described above. The results
are shown in Table 14 and Figs. 10 and 11.

On the other hand, the observation by ESCA revealed
5 that the valence of titanium is +4 from the value of bound
energy. Since no splitting occurred on 3p peak for
titanium and 2p peak for aluminum, there was no
interaction between titanium and aluminum. Namely,
titanium dioxide solely existed without interacting
10 between titanium and aluminum. When the surface of the
titanium dioxide-containing alumina hydrate was etched,
the amount of titanium was decreased to half in the
etching time of 100 seconds. No titanium was detected in
the etching time of 500 seconds. Therefore, it was
15 confirmed that the titanium dioxide exists only in the
vicinity of the surface of the alumina hydrate.

Recording media were obtained in the same manner as
in Examples 1 to 4 except that the titanium dioxide-
containing alumina hydrates were respectively used. The
20 physical property values of their ink-receiving layers and
evaluation results of the recording media are shown in
Table 15. The evaluation was conducted in accordance with
the following standards:

Printability:

25 Using an ink-jet printer equipped with four
recording heads for yellow, magenta, cyan and black inks,

1 each of said heads having 128 nozzles in a proportion of
16 nozzles per mm, ink-jet recording was conducted with
the inks of the ink composition 1 described in Examples 1
to 4, thereby evaluating the recording media in ink-drying
5 ability (absorptiveness), optical density of an image,
bleeding and beading.

(1) Ink-drying ability:

After single-color or multi-color solid printing was
conducted with the yellow, magenta, cyan and black inks,
10 the recorded area of each recording medium was touched
with a finger to determine the drying condition of the
inks on the surface of the recording medium. The quantity
of ink in the single-color printing was determined as 100
%. The ink-drying ability was ranked as A where none of
15 the inks adhered to the finger in an ink quantity of 200
%, B where none of the inks adhered to the finger in an
ink quantity of 100 %, or C where any ink adhered to the
finger in an ink quantity of 100 %.

(2) Optical density:

20 Solid printing was conducted with the black ink.
The optical density of the image formed was determined by
means of a Macbeth reflection densitometer RD-918.

(3) Bleeding and beading:

After single-color or multi-color solid printing was
25 conducted with the yellow, magenta, cyan and black inks,
the recording media were visually evaluated by whether

1 bleeding or beading occurred on their surfaces. The
quantity of ink in the single-color printing was
determined as 100 %. The resistance to bleeding or the
resistance to beading of the recording media was ranked as
5 A where bleeding or beading did not occur in an ink
quantity of 200 %, B where bleeding or beading did not
occur in an ink quantity of 100 %, or C where bleeding or
beading occurred in an ink quantity of 100 %.

Examples 27 and 28:

10 Aluminum dodeoxide was prepared in the same manner
as in Examples 25 and 26. The aluminum dodeoxide was
hydrolyzed in the same manner as in Examples 25 and 26 to
prepare an alumina slurry. The aluminum dodeoxide and
isopropyltitanium (product of Kishida Chemical Co., Ltd.)
15 were mixed at a mixing ratio of 100:5 by weight. Using
the alumina slurry as a nucleus for crystal growth, the
mixture was hydrolyzed in the same manner as in Examples
25 and 26 to prepare a titanium dioxide-containing alumina
hydrate slurry. Water was added to the alumina slurry
20 until the solid content of alumina hydrate was 7.9 %. The
pH of the alumina slurry was 9.5. A 3.9 % nitric acid
solution was added to adjust the pH of the slurry.
Colloidal sols were obtained under their corresponding
aging conditions shown in Table 13. Each of these
25 colloidal sols was spray-dried at 75°C to obtain its
corresponding alumina hydrate. As with those obtained in

- 1 Examples 25 and 26, the alumina hydrate was non-crystal
and was in the form of a flat plate. The physical
property values of the alumina hydrates were measured in
accordance with the respective methods described above.
- 5 The results are shown in Table 14. As with those obtained
in Examples 25 and 26, the titanium dioxide existed only
in the vicinity of the surface of the alumina hydrate.

Recording media were obtained in the same manner as
in Examples 1 to 4 except that the titanium dioxide-
10 containing alumina hydrates were respectively used. The
physical property values of their ink-receiving layers and
evaluation results of the recording media are shown in
Table 15. The evaluation was conducted in accordance with
the same methods as those used in Examples 25 and 26.

15 Table 13

Aging condition	Sample			
	Ex. 25	Ex. 26	Ex. 27	Ex. 28
pH before aging	5.6	6.9	6.9	7.3
Aging temperature (°C)	110	150	40	50
20 Aging period	8 hours	4 hours	4 weeks	3 weeks
Aging apparatus	Auto- clave	Auto- clave	Oven	Oven

Table 14

Item determined	Sample			
	Ex. 25	Ex. 26	Ex. 27	Ex. 28
Titanium dioxide content (ICP, % by weight)	0.150	0.140	0.150	0.140
Bound energy (eV)	459	459	459	459
Titanium dioxide content (ESCA, % by atom number)	0.02	0.02	0.02	0.02
Titanium dioxide content after etching of the surface				
100 seconds	0.01	0.01	0.01	0.01
500 seconds	0.00	0.00	0.00	0.00
Average particle size (nm)	45.0	35.0	40.0	30.0
Aspect ratio	3.5	8.3	3.5	8.1
Slenderness ratio	0.7	0.7	0.7	0.7
BET specific surface area (m ² /g)	76	134	70	140
Average pore radius (Å)	130	80	70	60
Half breadth (Å)	100	60	20	20
Peak 1 of pore distribution (Å)	130	80	120	140
Peak 2 of pore distribution (Å)	---	---	40	50
Pore volume (cc/g)	0.57	0.55	0.57	0.55
Volume ratio of peak 2 (%)	---	---	5	10
Relative pressure difference (ΔP)	0.03	0.10	0.03	0.10
Number of OH groups (groups/g)	1.6x10 ²⁰	1.7x10 ²⁰	1.9x10 ²⁰	1.5x10 ²⁰
Zeta-potential (mV)	20	17	20	17
Nitrate anion (% by weight)	0.1	0.5	0.1	0.5
Dispersion viscosity				
15 % by weight	17	15	18	13
20 % by weight	40	70	53	83
25 % by weight	420	458	445	460

Table 15

Item determined	Sample			
	Ex. 25	Ex. 26	Ex. 27	Ex. 28
Average pore radius (Å)	125	90	75	65
Half breadth (Å)	95	50	20	20
Peak 1 of pore distribution (Å)	130	80	140	150
Peak 2 of pore distribution (Å)	---	---	50	70
Volume ratio of peak 2 (%)	---	---	5	10
Pore volume (cc/g)	0.53	0.50	0.53	0.50
(cc/m ²)	9.0	8.4	9.0	8.4
Relative pressure difference (ΔP)	0.03	0.02	0.03	0.02
Printability:				
Drying ability	A	A	A	A
Optical density	1.71	1.72	1.71	1.70
Bleeding	A	A	A	A
Beading	A	A	A	A

Examples 29 to 32:

Each of the alumina hydrate dispersions prepared in Examples 25 to 28 and the polyvinyl alcohol dispersion as described in Example 25 were weighed out to give a weight ratio of 15:1 in terms of solids and mixed with each other. The resultant mixture was stirred to obtain a mixed dispersion. The mixed dispersion was applied by an air knife coating process to one side of a wood free paper web (Shiraoui 157, product of Daishowa Paper Manufacturing Co., Ltd.) at a rate of 20 g/m² to form an ink-receiving

1 layer. The evaluation results of the recording media are shown in Table 16. The evaluation was conducted in accordance with the same methods as those used in Examples 25 to 28.

5 Table 16

Item determined	Sample			
	Ex. 29	Ex. 30	Ex. 31	Ex. 32
Printability:				
Drying ability	A	A	A	A
Optical density	1.65	1.67	1.65	1.66
Bleeding	A	A	A	A
Beading	A	A	A	A

10 Examples 33 to 36:

Recording media were obtained in the same manner as in Examples 9 to 12 except that the alumina hydrates prepared in Examples 25 to 28 were respectively used. Printing was conducted on the thus-obtained recording media to evaluate their printability in accordance with the above-described standards. The evaluation results are shown in Table 17.

Table 17

Item determined	Sample			
	Ex. 33	Ex. 34	Ex. 35	Ex. 36
Printability:				
Drying ability	A	A	A	A
Optical density	1.08	1.07	1.08	1.09
Bleeding	A	A	A	A
Beading	A	A	A	A

The recording media according to the present invention and the ink-jet recording method making use of these recording media have the following advantageous effects.

In the first aspect:

1) Individual dyes and solvent components in inks were selectively adsorbed to pores having a specific radius. Therefore, when a medium having wide pore radius distribution is used, printability becomes hard to be affected by the composition of ink. Accordingly, selectivity to the composition of ink becomes higher.

2) Since the recording media have no hysteresis, the solvent component in an ink is easy to be desorbed. Therefore, the ink-drying ability of the media is improved, and so bleeding and setoff can be prevented.

3) When alumina in the form of a flat plate is used, the spaces among its particles can be widened if the closest packing is adopted. Therefore, there can be

1 obtained a medium having pores considerably wide in pore
radius distribution.

4) Since the alumina hydrate has good
dispersibility, the viscosity of a dispersion can be kept
5 low if the solids concentration of the dispersion is high.

5) Since the alumina hydrate has good
dispersibility even at a neutral region near pH 7, the
amount of an acid added to the dispersion can be
decreased.

10 In the second aspect:

1) Since the individual pigments or ink-receiving
layers have at least two peaks in pore radius
distribution, the function of the pores can be divided.

2) Since a dye in an ink is effectively adsorbed to
15 pores having a relatively small radius, images good in
resolution and sufficient in optical density can be
provided.

3) Since a solvent component in the ink can be
quickly absorbed in pores having a relatively large
20 radius, images free of beading, bleeding and running of
the ink and good in resolution can be provided.

4) Since the recording media have no hysteresis,
the solvent component in the ink is easy to be desorbed.
Therefore, the ink-drying ability of the media is
25 improved, and so bleeding and setoff can be prevented.

5) When alumina in the form of a flat plate is

1 used, the spaces among its particles can be widened if the
closest packing is adopted. Therefore, there can be
obtained a medium having pores considerably wide in pore
radius distribution.

5 6) Since the alumina hydrate has good
dispersibility, the viscosity of a dispersion can be kept
low if the solids concentration of the dispersion is high.

7) Since the alumina hydrate has good
dispersibility even at a neutral region near pH 7, the
10 amount of an acid added to the dispersion can be
decreased.

In the third aspect:

1) Both dye-adsorbing ability and dispersibility
can be improved by containing titanium dioxide in the
15 alumina hydrate. Since the viscosity of the dispersion
can be kept low even if the solids concentration of the
dispersion is high, the coating thickness of the ink-
receiving layer can be thickened. Further, since the
adsorption and fixing of an ink upon printing can be
20 improved, changes with time can be prevented.

2) When alumina in the form of a flat plate is
used, the spaces among its particles can be widened if the
closest packing is adopted. Therefore, there can be
obtained a medium having pores considerably wide in pore
25 radius distribution.

3) Since the alumina hydrate has good

1 dispersibility, the viscosity of a dispersion can be kept
low if the solids concentration of the dispersion is high.

4) Since the alumina hydrate has good
dispersibility even at a neutral region near pH 7, the
5 amount of an acid added to the dispersion can be
decreased.

5) Since titanium dioxide is colorless, the ink-
receiving layer is not colored even when it is added.

6) Individual dyes and solvent components in inks
10 were selectively adsorbed to pores having a specific
radius. Therefore, when a medium having wide pore radius
distribution is used, printability becomes hard to be
affected by the composition of ink. Accordingly,
selectivity to the composition of ink becomes higher.

15 7) Since the individual titanium dioxide-containing
alumina hydrates or ink-receiving layers have at least two
peaks in pore radius distribution, the function of the
pores can be divided. Since a dye in an ink is
effectively adsorbed to pores having a relatively small
20 radius, images good in resolution and sufficient in
optical density can be provided. Since a solvent
component in the ink can be quickly absorbed in pores
having a relatively large radius, images free of beading,
bleeding and running of the ink and good in resolution can
25 be provided.

8) Since the recording media have no hysteresis,

1 the solvent component in the ink is easy to be desorbed.
Therefore, the ink-drying ability of the media is
improved, and so bleeding and setoff can be prevented.

While the present invention has been described with
5 respect to what is presently considered to be the
preferred embodiments, it is to be understood that the
invention is not limited to the disclosed embodiments. To
the contrary, the invention is intended to cover various
modifications and equivalent arrangements included within
10 the spirit and scope of the appended claims. The scope of
the following claims is to be accorded to the broadest
interpretation so as to encompass all such modifications
and equivalent structures and functions.

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